



Leaching of a limonitic laterite in ammoniacal solutions with metallic iron

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ABSTRACT

The leaching of a limonitic laterite (containing approximately 1% Ni, 0.1% Co and 50% Fe) was studied in ammoniacal solution. The laterite was leached in the presence of metallic iron which acted as a reductant. The kinetic parameters studied included the effect of temperature, metallic iron concentration, total ammonia concentration and ammonium sulphate to ammonium hydroxide ratios. Tests were performed in a batch cell with temperature ranging from 50 to 80 °C at atmospheric pressure. The kinetic behavior for nickel and cobalt extraction was observed to be different. Cobalt extraction was initially faster than nickel and it showed good extractions at lower temperatures, however, after reaching a maximum value of approximately 80%, extraction decayed by as much as 50%. This was likely due to cobalt co-precipitation and/or adsorption into iron and/or manganese oxides and hydroxides which could form during the process. Cobalt losses tended to increase with temperature, total ammonia concentration, ammonium hydroxide to ammonium sulphate ratio and metallic iron concentration. Nickel extraction was increased by higher temperature, total ammonia concentration and metallic iron concentration up to a maximum of roughly 70% after 48 h at 80 °C. Through feed and solid residue analysis, by X-ray diffraction and SEM, it was possible to characterize and understand how the feed mineral reduction occurred. The main phases present in the feed and residue were goethite and magnetite, respectively. Results suggest that the reduction occurs through two main reactions. First, the reaction between goethite and metallic iron produced Fe(II) amines. The Fe(II) amines are capable of reducing goethite and producing magnetite. The Fe(II) amines play an important role because they accelerate the reduction and favor the extraction kinetics of nickel. The main advantage of using metallic iron as a reducing agent is the possibility of generating an autocatalytic system.

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1. Introduction

The hydrometallurgical treatment of limonitic laterite minerals is increasingly important as it is expected that the future of nickel and cobalt production will occur mostly through hydrometallurgical processes (McDonald and Whittington, 2008a,b). Several studies have been performed with a view to extracting nickel and cobalt in ammoniacal media at near neutral pH (Kerfoot and Weir, 1988). However, limonitic minerals cannot be directly leached under these conditions as they must first be reduced in order to release Ni(II) and Co(II) to solution.

The Caron process for the extraction of nickel and cobalt in ammoniacal solution was first used in 1942. This process includes a reductive roasting stage followed by oxidative ammoniacal leaching and presents some limitations such as high operational costs; mainly from the drying and roasting stages. It is also known to have poor cobalt extractions (about 50%) probably associated with either the adsorption of cobalt onto ferric hydroxides, which are precipitated during the leach,

or the passivation of the Fe–Ni–Co alloys formed during the reduction step (Kerfoot and Weir, 1988; Monhemius, 1987; Nicol et al., 2004).

Also, a large amount of research has been conducted on acid leaching: this includes pressure acid leaching (general conditions 245–270 °C) or very high acidity atmospheric leaching (~100 °C) to release nickel from goethite. In general, acid leaching processes have high recoveries for nickel and cobalt but they are subject to acid consumption issues and leach liquors usually require neutralization prior to further treatment (McDonald and Whittington, 2008a,b). On the other hand, ammonia has several advantages as a leaching agent: it has low toxicity, low cost, high selectivity and does not require expensive reactor materials. It can also be regenerated (Meng and Han, 1996).

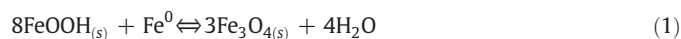
This work reports experimental results obtained during the leaching of a limonitic laterite in ammoniacal solutions using metallic iron as a reducing agent at atmospheric conditions. A previous conference article reported limited results which investigated such experimental variables as agitation, percent solid in leach, temperature, total ammonia concentration and metallic iron concentration (Zuniga and Asselin, 2009). Based on our previous work, the objective of this paper is to understand the kinetics of this leaching option and expand on our discussion of the leaching process by providing further information as to the effects of metallic iron particle size, different ratios of ammonium

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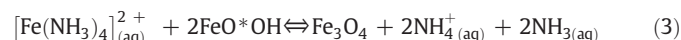
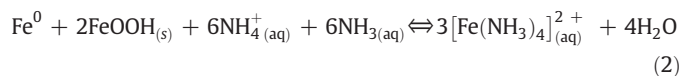
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sulphate to ammonium hydroxide in the leach, the effect of ammonia losses during the leach and the nature of the residues and associated pay metal losses. Furthermore, certain experimental variables and conditions are clarified herein and additional data are considered.

The proposed mechanism for goethite reductive leaching with metallic iron is described, where the overall chemical reaction is:



This reaction may occur in two stages in ammoniacal media:



The first stage reaction is between solids, i.e. a galvanic reaction in ammoniacal media where the metallic iron is dissolved (anodic reaction), the goethite is reduced and both are converted into Fe(II) amines— $\text{Fe}(\text{NH}_3)_n^{2+}$. In the second stage Fe(II) amines also reduce goethite to magnetite (Das and Anand, 1995). Mohapatra et al. have studied synthetic goethite reduction to magnetite using ferrous sulphate as a reducing agent in ammoniacal media at ~130 °C. The main focus of this study was the conversion of goethite to magnetite but the mechanism of the leaching reaction was unclear (Mohapatra et al., 2002).

Considering kinetic factors, it is possible that the reaction between solids is slower. Indeed, galvanic contact is not expected to achieve complete utilization of the added metallic iron, and hence complete reduction of the goethite is not expected. This is due to the possible loss of galvanic coupling upon progress of reaction together with the consumption of the anodic reagent (metallic iron).

The advantage of having a reaction between solids is the generation of an autocatalytic process through which Fe(II) amines are generated and can, in turn, act as reductants. When nickel and cobalt are leached in ammoniacal solution they are also complexed with ammonia to form amines:



Based on the Pourbaix diagrams for the Ni–NH₃–H₂O and Co–NH₃–H₂O systems, mono- to hexa-ammines of nickel and cobalt (i.e. $1 \leq n \leq 6$) can form depending on pH and total ammonia concentration (Asselin, 2008; Isaev et al., 1990; Osseo-Asare, 1981a,b; Osseo-Asare and Asihene, 1979; Zhong and Hepworth, 1995).

2. Experimental procedures

The samples were prepared as follows: 14 kg of limonitic laterite containing approximately 37 wt.% water were dried. The grain size was below ~52 µm. The sample was homogenized by using a ring mill and coning and quartering procedure. One representative sample of approximately 3 kg was obtained. Further splitting by coning and quartering was performed to produce samples which were used in the leaching tests. The samples were characterized by chemical analysis (ICP-AES), SEM and quantitative X-ray diffraction (QXRD) using the Rietveld method. Selected elements present in the laterite are given in Table 1. Table 2 shows the crystalline phases found in the laterite as obtained through QXRD.

Experiments were done batch-wise in a 2 L jacketed and baffled glass reactor under atmospheric pressure where the reactor was sealed with a PTFE lid and a reflux condenser was the only gas outlet.

Table 1
Chemical analysis of the laterite feed material.

Elements	Content (mass %)
Iron	50.0
Nickel	1.00
Cobalt	0.10
Zinc	0.05
Copper	0.02
Manganese	0.80

The impeller used was a 45° pitched-blade turbine. The chemical reagents were of analytical grade and were used as-received while deionized water was used to make the solutions. Temperature was controlled by circulation of hot water (thermostatically controlled water bath) through the reactor's water jacket. Leach solutions were prepared using ammonium hydroxide and ammonium sulphate. The pH was always set above the buffer point of ammonia (which changed with temperature) to ensure the stability of aqueous ammonia and the nickel, cobalt and iron amines. The pH was also adjusted to reduce the influence of metal ion adsorption (especially cobalt) onto oxides and hydroxides according to recommendations found in the literature (Esmadi and Simm, 1995; Osseo-Asare and Fuerstenau, 1979, 1980a,b, 1987). The test solutions and reactor head space were purged with nitrogen gas using a sparger (15 ml/min) for 15 min before heating the solution, to decrease the presence of oxygen and favor the formation of Fe(II) amines rather than hydroxides. Samples were taken throughout each test (14 ml approximately of pulp). It is important to mention that when the samples were not under the reducing conditions which prevailed in the reactor, the formation of Fe(III) hydroxides was favored. For this reason, conventional separation procedures are not applicable in this case. The samples were separated quickly using a centrifuge followed by filtering using 1 micron particle size retention paper. The clean solution was then acidified with 2 M hydrochloric acid and analyzed by AAS, XRF and ICP-AES. Total volume at the end of each test was always measured. For atomic absorption analysis samples were diluted into a 5 wt.% hydrochloric acid solution. The leach residues were dried at room temperature then homogenized in order to take representative samples.

3. Results and discussion

The effects of agitation (150 to 350 rpm) and percentage of solids (10 to 20%) have already been reported (Zuniga and Asselin, 2009). With a metallic iron particle size below 10 µm, best results were obtained at 250 rpm stirring speed and 15% solids. These test conditions were retained for all subsequent experiments reported here. In most leaching processes it is important to keep particles suspended, so that they are in better contact with the leaching agent. However, in the case where there is a solid to solid reaction which is of galvanic nature, contact between particles is of obvious importance. Excessive agitation could be detrimental for this process since it could interrupt physical contact between the particles thus slowing down or even stopping the reduction of goethite.

Table 2
Quantitative phase analysis of laterite feed (wt.%).

Minerals	Ideal formula	Laterite (%)
Goethite	$\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$	59.0
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	12.6
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	5.70
Ferrihydrite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	19.5
Gibbsite	$\text{Al}(\text{OH})_3$	0.90
Kaolinite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	2.30

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